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The use of photomultipliers in spectroscopy

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With 9 figures in the text

In this paper we have investigated some characteristics of photomultipliers in connection with their use in spectroscopic research. The automatic recording is done by a scanning method. The mechanical construction, which is very simple, can be applied directly to an ordinary spectrograph designed for photographic recording. Some different objects have been investigated, and the efficiency of the photoelectric method as a supplement to the photographic is discussed.

I. Introduction

The use of the photoelectric cell as a detector in spectroscopic investigations in the optical wavelength region has increased very much during the last few years by introduction of the commercial photomultiplier.

Though all the results, which can be reached with the multiplier could probably also be arrived at using a common photoelectric cell, the complicated techniques of measurement, which must be used with the latter, have prevented a more general use of the photoelectric cell in spectroscopy.

A large number of papers have been published describing the use of the multiplier in chemical and metallurgic spectroscopic analysis, but rather little work has been done showing the efficiency of the multiplier as a valuable aid in addition to the photographic plate in a spectroscopic research laboratory.

The most comprehensive investigation in this direction seems to have been carried out by DIEKE and CROSSWHITE (1) at the John Hopkins University, Baltimore.

A special domain in which photomultipliers have been used on a large scale is the Raman-spectra (2).

The multiplier has also been used together with an oscilloscope to study the intensity variations of spectral lines in discharges, arcs and sparks as a function of time (3).

II. The photomultiplier

The RCA-cells

In our experiments we have used RCA multipliers. The 9-stage multipliers are available in four different types, all of which have the same geometrical mounting. The 931 A is a standard cell with a sensitivity maximum at 4 200 Å. The IP 21 cells are 931 A in type but specially selected for their high sensitivity and amplification and low dark current. The IP 22 has a sensitivity region somewhat extended towards the red, but this is in other respects inferior to the other cells. The IP 28, which is furnished with special glass, is sensitive down to 2 100 Å.

RCA has recently placed on the market a 10-stage multiplier (5819) specially designed for scintillation counters. It has S 9 response with its sensitivity maximum at λ 4 800 Å. We have not yet had an opportunity to try out this cell. At normal working voltages it has lower amplification than the other cells, but its large cathode area may possibly be advantageous especially when a diffusing screen is used between the exit slit of the spectrograph and the cell.

Linearity

The collector current in a photomultiplier has generally, in accordance with the nature of photoelectric and secondary emission been assumed to be proportional to the illumination on the photocathode. It is difficult to prove this assumption experimentally with a high degree of accuracy. The only one who seems to have made a thorough investigation of the linearity is Engstrom (4). He found, with an experimental accuracy of 3 %, that the anode current is linear in the range 10^{-9}—10^{-3} amp. Stronger currents lead to a saturation in the output current caused by space charges which distort the electric field in the tube. For small currents say less than 10^{-6} amp, there is no reason to doubt that the linearity is sufficient for practical purposes.

Too strong an illumination will give rise to a fatigue effect in the sensitivity of the cell. Though the multiplier still reacts linearly, the change in sensitivity during the registering of a spectrum will disturb the intensity determinations.

Too large resistances in the voltage divider of the dynodes or too large an output resistance in the anode circuit will, when strong currents pass through the tube, cause the potentials of the electrodes to vary with the illumination. When using an amplifier behind the multiplier the linearity range will generally be limited by the amplifier.

We have investigated the linearity with our photocell mounting and amplifier using a method based on the inverse quadratic distance law. Within the experimental accuracy no deviations from the linearity were found in the intensity range, used later in our measurements.

Fatigue

The fatigue effect, which sets in at high photocurrents, is caused by the violent electron bombardment of the last dynodes. Dieke (1) and Engstrom (4) have investigated the effect more closely and both of them find that the fatigue is negligible for anode currents less than 1 μA.

In our measurements we always used very small currents and never had any trouble with this effect. It does not seem to be necessary when using weak illumination to take any further precautions apart from controlling the reproducibility of the measurements.

Noise and dark current

The great advantage of using a multiplier over an ordinary photoelectric cell is that an amplification of the order of 10^6-times the electron current from the photocathode is obtained very conveniently without any appreciable reduction of the ratio signal to noise. The limit of serviceableness is set by the statistical fluctuations in the thermionic electron current from the photocathode which, according to ENGSTROM (4), is of the order of 10^{-14} amp at room temperature. The factor by which the quadratic shot noise in this component of the dark current and also in the photoemission is multiplied during the passage through the tube is $\frac{G^{2n+1}-G^n}{G-1}$ (G = Gain per stage, n = number of stages) (5). In a nine stage multiplier at an amplification of $G^n = 10^6$ this will lead to a reduction in the primary signal to noise of about 12 %. The thermionic emission from the dynodes will add only a few percent to the dark current from the photocathode. For a rough calculation of the noise in the tube it is therefore sufficient to use the common formulae for the shot noise:

$$\overline{i_n^2} = 2\,e\,i\,\Delta f$$

where i is the component in the output current coming from the thermionic emission — and photo-emission from the photocathode, $\overline{i_n^2}$ is the quadratic mean of the fluctuations in the current i, e is the electronic charge, and Δf is the frequency range limited by the measuring device.

For measuring the direct current from the multiplier we used an electrometer tube amplifier with a grid resistance of $10^7\ \Omega$. The output current from the amplifier was registered by a galvanometer with a delay constant of 0.7 sec.

In this method of measurement, the part of the dark current which consists of ohmic leakage in or outside the cell and which does not contribute to the noise, may also cause trouble on account of its varying strength. The outside leakage can of course be eliminated by a suitable method, but there will still remain the leakage on the inside of the glass envelope caused by traces of conductive materials. At low amplifications the dark current consists principally of this ohmic leakage. When using a direct current amplifier the stable part of the dark current may be compensated.

In order to study the origin of the dark current in our measurements with the IP 21, we shall make a calculation for the thermionic emission from the photocathode. If we assume that the observed fluctuations in our dark current emanate from the thermionic emission from the photocathode, the total emission i from the latter can be determined from the formulae for the shot noise.

The fluctuations in the galvanometer reading were of the order of ½ mm when the output-current from the multiplier was amplified about 30 times in the direct current amplifier. Such an additional amplification will not introduce any extra noise. A deflection of the galvanometer of 1 mm corresponds to a current of $7 \cdot 10^{-10}$ amp and the amplification in the multiplier tube is about $2 \cdot 10^6$ with a dynode voltage of 100 V. The fluctuations in the dark emission from the photocathode is then $(\overline{i_n^2})^{\frac{1}{2}} = 6 \cdot 10^{-18}$ amp.

The dark emission i is obtained from this shot noise by introducing the equivalent band width of the galvanometer ($\frac{1}{3}$ sec^{-1}) in the formulae for the shot noise. This gives for i the value $3 \cdot 10^{-16}$ amp, which means an output current of $6 \cdot 10^{-10}$ amp.

The output dark current measured was of the order of $7 \cdot 10^{-10}$ amp which makes it probable that we had no ohmic leakage comparable with the dark emission. This is also in accordance with Engstrom's statement that for high dynode voltages the thermionic current dominates over the inner leakage. Our value ($3 \cdot 10^{-16}$ amp) for the thermionic emission from the photocathode is lower than Engstrom's (10^{-14}) for the 931 A. It seems probable that the IP 21 selected has a dark emission appreciably lower than that of 931 A.

Cooling of the cell has been used extensively, for example by RANK (2), ENGSTROM (4) and DIEKE (1). There is a striking reduction in the ratio noise/signal on lowering the temperature. The cooling can be performed with liquid air, dry ice or even by a cooling plunge into running water. When cooling with liquid air at least there are great experimental difficulties owing to the condensation of water vapour which will cause electrical leakage. The fatigue effect seems to be more appreciable at low temperatures (6).

III. The spectrograph

Type and dimensions

When using photographic recording the choice of spectrograph is determined by the nature of the object to be studied. When a high resolving power is necessary a spectrograph of large dimensions is preferable, and a smaller one with large aperture when the weakness of the object makes this necessary or when the main purpose is to get a large part of the spectrum in one exposure. This is not, however, the case with the direct registering method, and there is nothing to be gained in intensity by using a smaller spectrograph. Moreover, it is easier to apply the mechanical device to a large spectrograph because of its greater dimensions and dispersion.

For allround purposes it is necessary to use a scanning method for the photoelectric cell. When the cell is to be applied to a common spectrograph designed for photographic recording it is probably most convenient to have the exit slit moving in the focal plane. The most severe drawback of this mechanical design is the movement of the image across the photocathode. When the spectrograph is especially constructed for photoelectric recording, the most suitable mechanical arrangement is probably of the type with a fixed exit slit used in infrared spectroscopy, for instance the Pfund type (7). There is, on the other hand, a great disadvantage in that the spectrograph cannot be used alternatively for photographic registering.

The intensity with the various concave grating spectrographs we used for photoelectric registering appears from the following consideration.

We assume that the image of the light source through the projecting lens covers the entrance slit of the spectrograph and that the grating is filled with light. The radiant power per unit projected area and per unit solid angle (the steradiancy) is called $S_{\Delta\lambda}$ within the wavelength range $\Delta\lambda$. Then the radiant power $P_{\Delta\lambda}$ which passes the spectrograph and is focused to the image is

$$P_{\Delta\lambda} = l \cdot b \cdot S_{\Delta\lambda} \cdot \omega \cdot G \tag{8}$$

l = length of the entrance slit
b = width of the entrance slit
ω = solid angle slit-grating
G = Grating factor — determined by the reflecting power of the grating in the given wavelength region and order.

We intend to compare the intensity in concave grating spectrographs of different dimensions and consider the following cases:

A) When the resolving power is the same for all the spectrographs.

B) When the highest resolving power is used in the spectrographs.

For purposes of comparison we also want to calculate

C) The relative intensity in the photographic case.

A: We assume that the natural width of the spectral line is small in comparison with the width which it obtains in passing the spectrograph, and call the steradiancy of the line S_λ. In order to get a satisfactory image, the slit should not make too large an angle at the grating Hence we can put $l \propto \varrho$ (ϱ is the radius of curvature of the concave grating). Above the limit used to obtain the full resolving power the half-width of a spectral line will increase proportionally to the slit-width. The resolving power is thus inversely proportional to the slit-width; and also directly proportional to the dispersion. For a given value of the resolving power we can put $b \propto \varrho \cdot n$ (n is the number of groves per unit lengths of the grating). The solid angle is $\omega \propto \frac{A}{\varrho^2}$ (A is the ruled area of the grating).

The radiant power transmitted through the spectrograph is:

$$P_\lambda \propto n \cdot A \cdot S_\lambda \cdot G.$$

B: We assume again the natural widths of the spectral lines to be small. The suitable slit-length is $l \propto \varrho$ and the solid angle $\omega \propto \frac{A}{\varrho^2}$. The suitable slit-width for high intensity without lowering the resolving power is $b = \frac{\varrho}{L} \cdot \lambda$ for noncoherent and $b = 2\frac{\varrho}{L} \cdot \lambda$ for coherent illumination of the slit (L is the width of the ruled part of the grating) (9). In practice the mode of illumination lies somewhere between these two extremeties and we can put $b \propto \frac{\varrho}{L} \cdot \lambda$.

The radiant power transmitted is:

$$P_\lambda \propto \frac{1}{L} \cdot \lambda \cdot A \cdot S_\lambda \cdot G = \lambda \cdot H \cdot S_\lambda \cdot G$$

(H is the length of the groves).

C: With the photographic plate the maximum blackening on the plate is determined by the radiant power per square unit in the core of the line. We write the total radiant power of the line transmitted $P_\lambda = b \cdot l \cdot S_\lambda \cdot \omega \cdot G$. We assume that we have the ideal width of the slit as regards resolution and intensity. Because of the astigmatism the intensity in the middle of the line will rise with the length of the slit up to a certain limit $l' = H(\sin^2\beta + \sin\alpha \operatorname{tg}\alpha \cos\beta)$ (7). (α is the angle of incidence and β the angle of diffraction). If we are beyond this limit, then the radiant power per unit length in the middle of the line will be $\frac{P_\lambda}{l}$. The half intensity width of the line is almost equal to b. The inverse of this will give the concentration of the radiant power in the core of the line along the focal curve. The radiant power per square unit at the centre of the line is thus

$$p_\lambda \propto S_\lambda \cdot \omega \cdot G = S_\lambda \cdot \frac{A}{\varrho^2} \cdot G\,.$$

In order to be able to compare two spectrographs with each other we must assume the mode of illumination and the grating factors to be the same. We will then have the following values for the brightness of the spectrum produced in a spectrograph in the three different cases:

$$\begin{array}{ccc} \text{A:} & \text{B:} & \text{C:} \\ P_\lambda \propto n \cdot A & P_\lambda \propto H & p_\lambda \propto \dfrac{A}{\varrho^2}\,. \end{array}$$

The numerical values for the three gratings we used in Eagle mounting are given in the following table:

			Grating		
			1 m	2 m	21 f
Radius of curvature	ϱ	cm	100	200	640
Number of groves	n	cm^{-1}	5 700	5 700	11 800
Ruled area	A	cm^2	29	65	79
Length of groves	H	cm	5.1	5.1	5.8
Theoretical resolving power (Cases B and C)			36 000	72 000	154 000
Rel. brightness produced					
A. photoel. Equal resolving power			1	2	6
B. » Full » »			1	1	1
C. photograph. Full » »			1	0.6	0.07

As is apparent from the above rather rough calculations a large spectrograph should be used in the photoelectric method and there is little need, in contradistinction to the photographic method, to change spectrographs according to the appearance of the object to be studied.

IV. The light source

When the scanning method is used to register different spectral lines, the lines will pass the exit slit at different moments so that it is necessary either to use stable light sources or to compensate the fluctuations in some way. This can be done, for instance, by fixing an extra cell on a line which has the same conditions of exitation and thus follows the fluctuations of the lines of which the relative intensity is to be investigated. The measuring circuit is then designed in such a way that it registers the ratio of the intensities falling on the two photocells.

In our experiments we have used only stable light sources as discharge tubes, hollow cathodes and tungsten lamps, but even here it is necessary in precission measurements to control the stability during the measuring unless it has been possible to stabilize the light source completely against fluctuations in the line voltage.

Dieke, Crosswhite (1) and Kessler, Wolfe (10) have used compensated measuring circuits successfully with such light sources as arcs and sparks. Crosswhite (11) reports a probable error of less than one percent in one investigation of the intensities of 1 200 iron lines from a direct current arc.

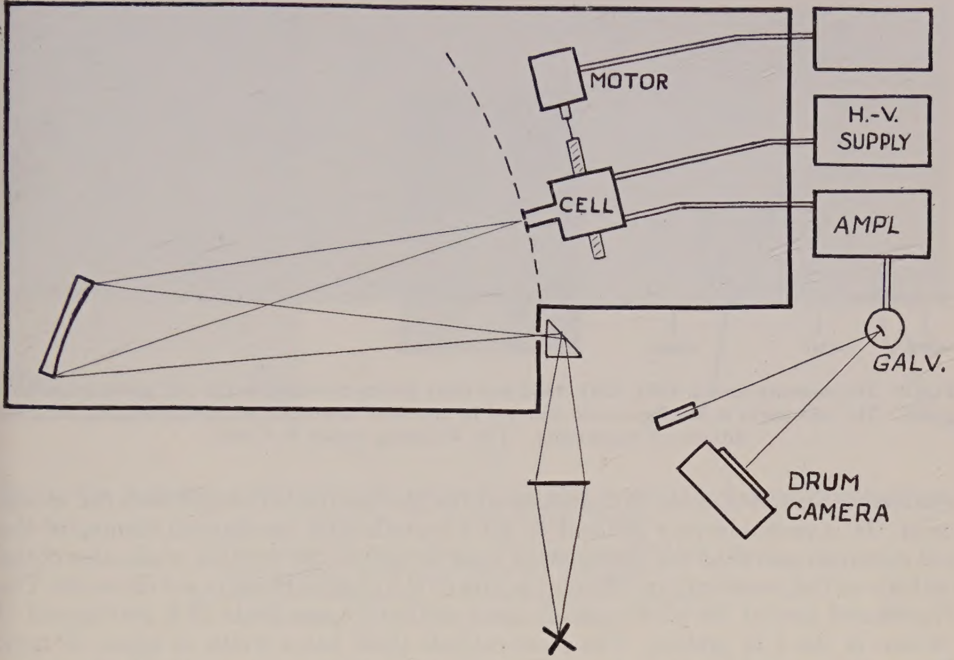


Fig. 1. The registering apparatus mounted in the 21 foot grating spectrograph.

V. The recording method

When the scanning method is to be used in a common spectrograph the mechanical device should be applied in such a way that the spectrograph can easily be used alternately for photographic recording. The two methods of registering supplement each other excellently in, for example, analyses of spectra. The photographic method is superior in determining wavelengths while the photocell gives the best values for the intensity of the lines. Fixed cells can of course also be used in a common spectrograph when studying single lines in, for instance, chemical spectroscopic analysis or for studying the conditions of exitation in a light source.

We have used the scanning method. The registering apparatus is shown in Fig. 1. The cell is mounted in a totally dark box furnished with a slit. During the registration the cell-container is driven by a precision-made screw in such a way that the slit moves in the focal plane. There are the following possibilities for adjusting the apparatus. The entire container can be turned so that the line photocathode-slit can be directed towards the grating. The slit is movable in the same direction and can be adjusted to the focal curve. Finally, it is possible to turn the slit in order to get it parallel to the spectral lines. The linear movement of the slit limits of course the range which can be scanned by the photocell without renewed adjustment. If a defocusing of ± 0.1 mm — which is less than the accuracy of adjustment of the spectrograph — is tolerable, then the range which can be scanned is 100 Å in the first order of the 21 foot grating spectrograph and 500 Å in that of the 1 meter one.

A more important disadvantage is that the line slit-photocathode does not turn

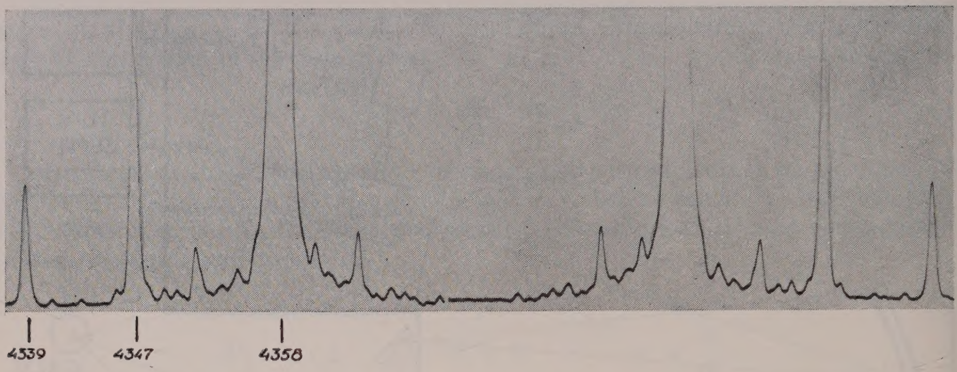


Fig. 2. The mercury lines λ 4358, 4347, 4339 and their ghosts recorded in the 1 m grating spectrograph. The two parts in the figure are scanned in opposite directions without changing the conditions of registering. The scanning speed 6 Å/min.

automatically and thus the illumination of the photocathode changes with the movement. It is probably very difficult to get a reproducable mechanical turning of the cell container and thus the illumination must be spread out over the whole area of the cathode as the sensitivity in different points of the photocathode is not the same. The illuminated area of the photocathode has a width of 4 mm in the 21 ft grating and of 10 mm in the 1 m grating. The photocathode itself has a width of about 10 mm. When the scanned length in the first order of the 21 ft grating is 100 Å, the image moves about 2 mm across the photocathode. The corresponding figure for 500 Å in the 1 m grating is 5 mm. The illumination may be further smoothed out by using a diffusing screen. As the mounting must be calibrated when making intensity measurements over a large range because, for example of the wavelength dependence of the cells, it is more handy not to have a turnable cell-container. The calibration is easily carried out with, for instance, a tungsten band lamp, the temperature of which is determined with a pyrometer.

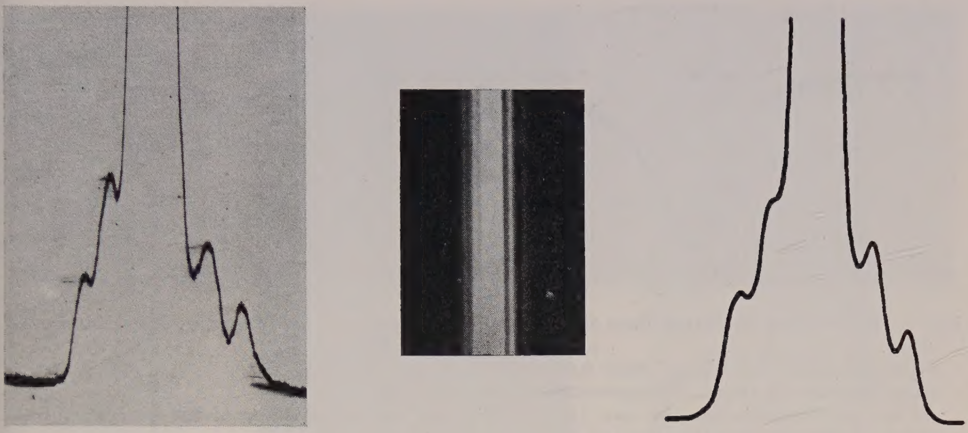
The driving screw is turned by a synchronous motor which gives a scanning speed of 3 mm per minute. The speed can be slowed down by a gear-box by a factor of 3, 9 or 27.

The multiplier is fed from a stabilized voltage supply of the Evans type (12), which stabilizes voltages between 600 and 1200 volt well. The voltage divider to the dynodes of the multiplier is placed on the outside of the cell-container. We have used anode batteries alternately, but could observe no advantages over the line-driven supply.

The current from the multiplier is amplified in a direct current amplifier of the du Bridge-Brown type, with the electrometer tube T 114 and an input resistance of 10^7 ohms. The maximum current-amplification is 130 times. The dark current of the cell is compensated in the amplifier.

The current is recorded photographically by means of a mirror galvanometer and a drum camera. The galvanometer most used has a sensitivity of $7 \cdot 10^{-10}$ amp/mm at a scale distance of 1 m.

Fig. 2 shows the reproducibility of the recording method.



a b c

Fig. 3. The hyperfine structure in the mercury line 4358 in the 21 foot grating spectrograph. Violet is to the left in the figures.

a) Photo-electric recording. Scanning speed 0.14 Å/min.
Entrance slit 0.02 mm. Exit slit 0.01 mm.
b) 40-times enlargement of photographic exposure.
c) Compilation of the microphotograms.

VI. Special objects

We chose several objects of quite different natures in order to study the resolution, the sensitivity and other characteristics of the multiplier apparatus as compared with the photographic plate.

The hyperfine structure of the mercury line 4358

In order to estimate the resolving power we made photo-electric and photographic recording of the mercury line 4358 in the 21 ft grating using the same light-source. We started by using a high frequency discharge as light-source. The transmitter was a 10 Mc push-pull oscillator. The discharge was very intense, and resolution of the components in the line slightly better than in the Geissler tube discharge later used. We did not, however, succeed in getting the discharge stable enough to make the results reproducible. Our intention was not so much to try to reach the absolute resolving limit of the spectrograph as to compare the efficiency of the photo-electric and photographic method when recording an object with narrow structure. For this reason we preferred to use a fairly stable Geissler tube driven on 2500 V and 65 mA alternating current.

Fig. (3 a) shows the hyperfine structure of Hg 4358 recorded by the photo-electric cell. Though the violet components of the line seemed to be separated in Fig. (3 b), which is a 40-times enlargement of the photographic plate, it is not possible to get them well resolved in the micro-photometer. Fig. (3 c) gives the diagrams in a Challonge photometer of ten different photographic exposures.

The reproductions show the difficulty of registering with a photographic plate such small intensity variations as these violet components on the wing of an intense line.

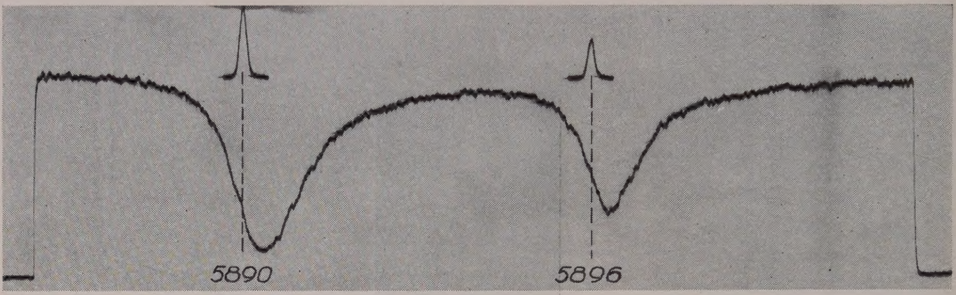


Fig. 4. The Sodium resonance lines 5890 and 5896 in absorption broadened by Xenon at a pressure of 2.8 atm (0° C).
Scanning speed 1.3 Å/min. Slits 0.05 mm.
Amplification 25 times. Temperature of the oven 250° C.
In the reproduction may be seen the red-shift and asymetric shape of the broadened lines generally accompanying this type of broadening.

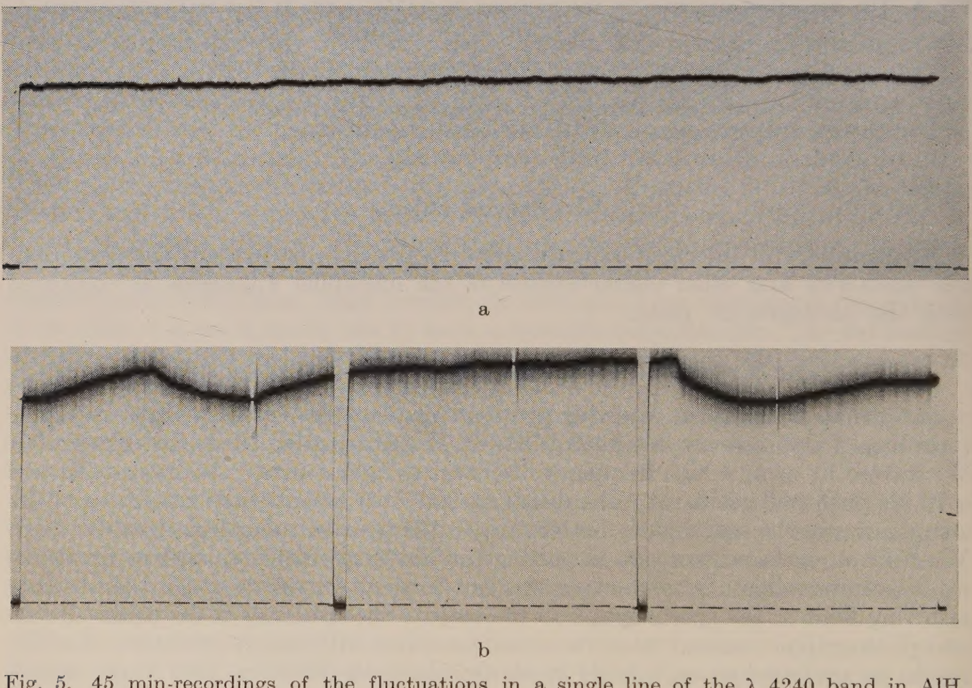


Fig. 5. 45 min-recordings of the fluctuations in a single line of the λ 4240 band in AlH.
a) Without changing the conditions during the recording.
b) The liquid air trap has been refilled.

There is no reason to believe that the resolving power of the photo-electric method is inferior to that of the photographic. The photo-electric method is nothing but a photometrizing directly in the spectrograph and with good mechanical equipment there might well be a small increase in resolution as a result of jumping over the complicated intermediate step, the photographic plate.

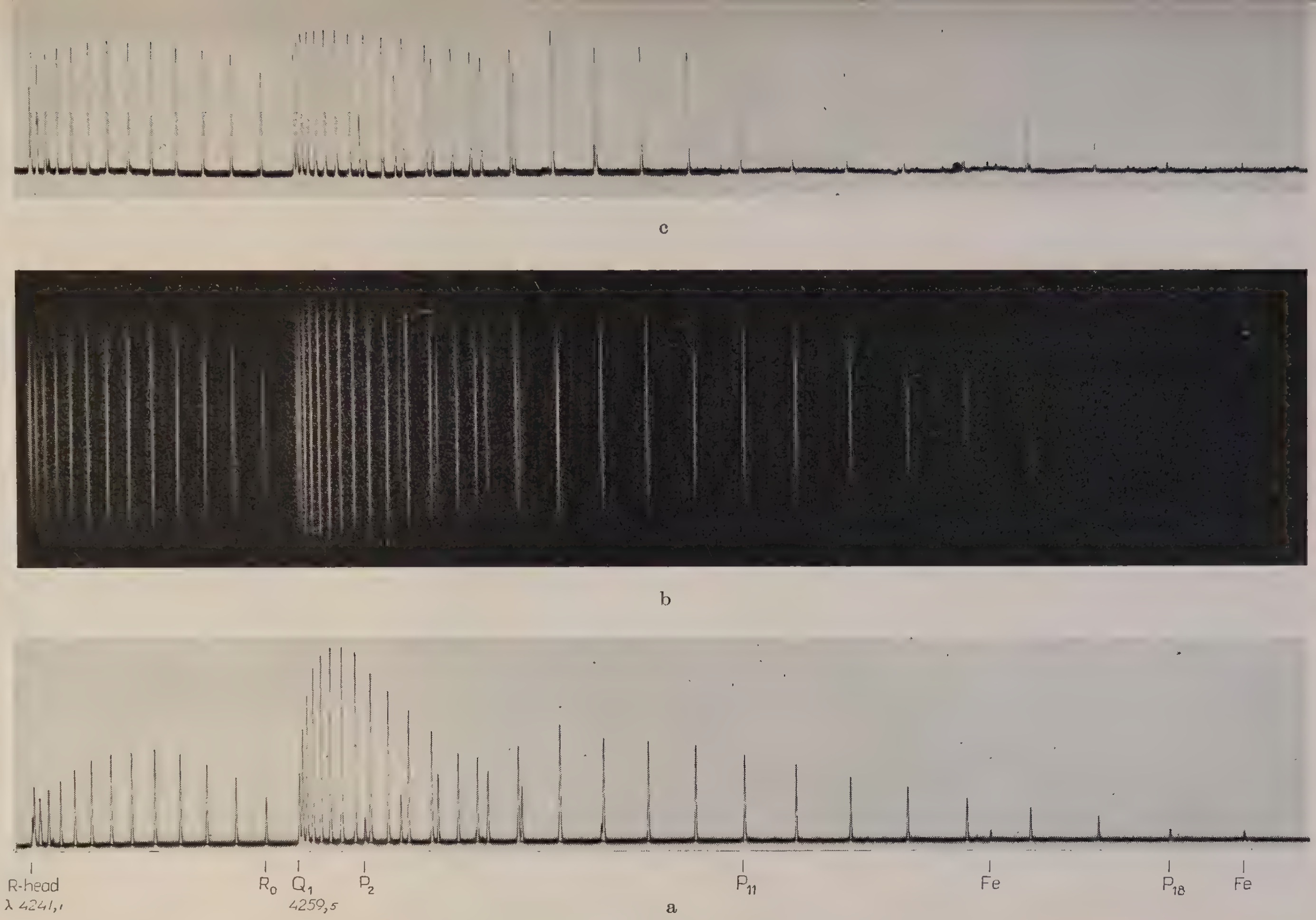


Fig. 6. The λ 4240 band of AlH.

a) Photo-electric recording. Scanning speed 1.3 Å/min. Slits 0.02 mm. b) Photographic exposure. Slit 0.02 mm. Exposure time 15 min. c) Microphotogram of b).

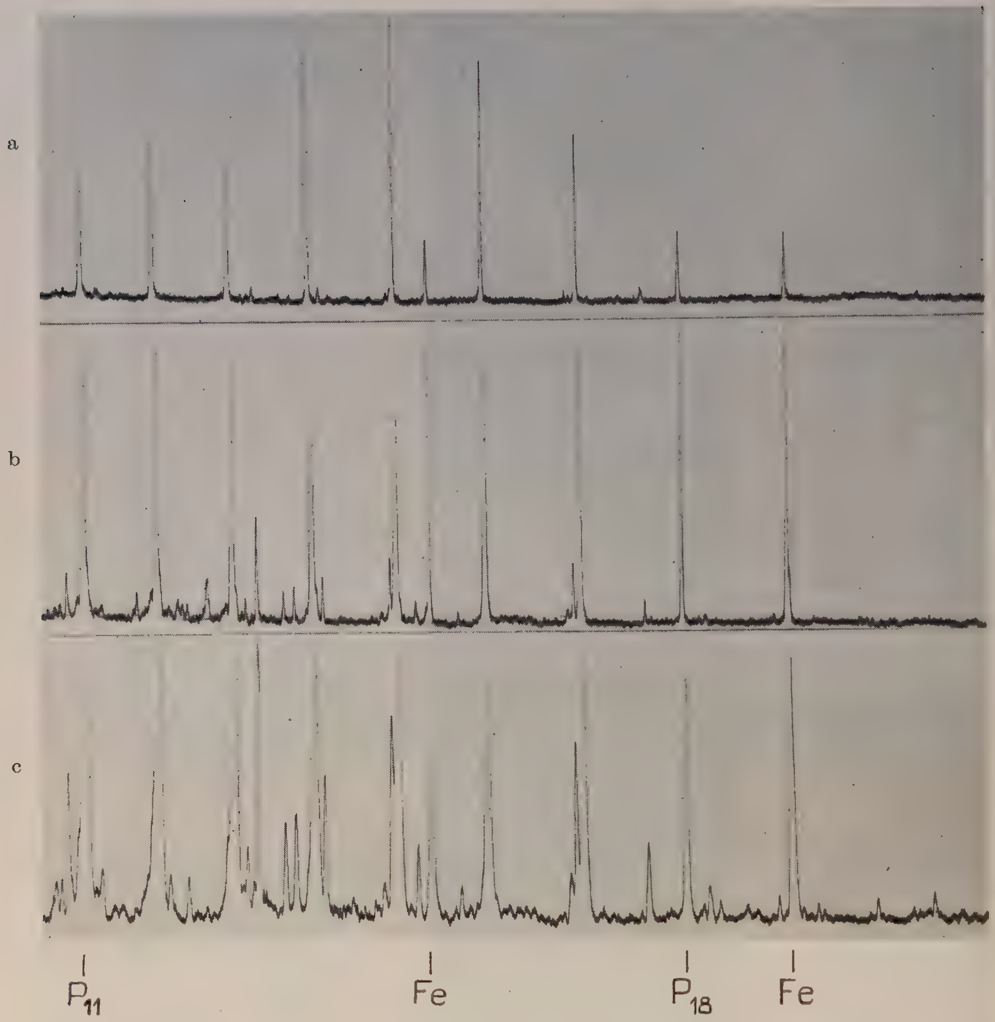


Fig. 7. The last lines of the P-branch of the band λ 4240. Photo-electric records with the slit widths.

a) 0.02 mm. b) 0.05 mm. c) 0.10 mm.

Scanning speed 1.3 Å/min. On the right wing of the Fe-line in fig. a) and b) the last line of the P-branch (nr 19) is to be seen.

The photoelectric method is much less tedious for an object similar to that described here than the photographic and may be given a high accuracy of measurement.

Na-absorption lines broadened by foreign gases

The possibilities of the photoelectric method have been tried out for studying absorption lines broadened by foreign gases. The experimental method was the same as that earlier described (13) except for the registering.

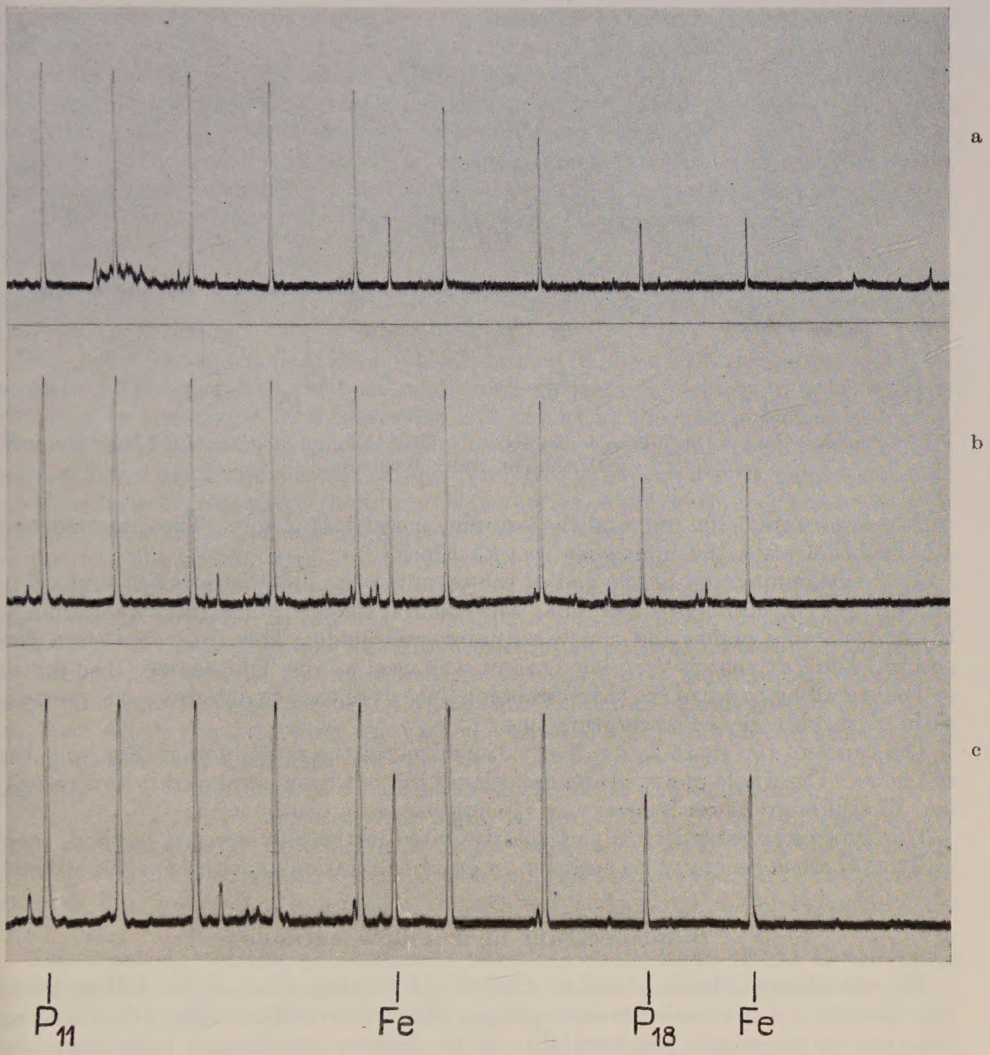


Fig. 8. The last lines of the P-branch of the band λ 4240. Microphotograms of exposures with the slit widths

a) 0.02 mm. b) 0.05 mm. c) 0.10 mm.

Exposure time 45 min.

The continuous light-source was a 180 W tungsten band lamp fed from a large accumulator. The alkali metal together with the rare gas was introduced into the pyrex tube which was then sealed off. The tube was then placed in an electric oven and heated to the desired temperature.

The Na-resonance lines broadened by Xenon were investigated in the 21 ft concave grating. The RCA IP 21 was used as detector, as this cell proved to be superior to the red sensitive IP 22 in this wavelength range as regards signal/noise. The slit

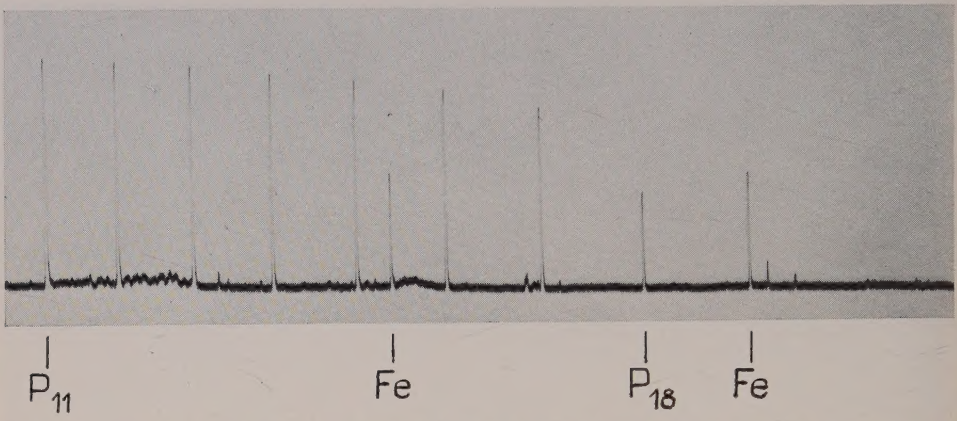


Fig. 9. The last lines of the P-branch of the band λ 4240. Microphotogram of a 2 hour exposure, with the slit width 0.02 mm.

widths used were 5/100 mm and the scanning speed 1.24 Å/min. The direct current amplification after the multiplier was 25 times.

At the beginning and at the end of the scanning the illumination was shut off in order to get the marks of a zero line. The cell and the recording drum were brought to their starting points and a new scanning was made. This time an Osram Na-spectral lamp driven on very low current was used as the light source. The marks on the recording paper of the sharp emission lines were used to determine the pressure shift of the broadened absorption lines.

The cause of the short period fluctuations seen in the reproduction (Fig. 4) is the cell noise. The whole power of the band lamp has not been employed in this recording. If still more power is necessary a pointolite lamp can be used.

This type of investigation is particularly suited to the photoelectric method, especially as there is generally no need for an extra calibration as with emission spectra.

Bandspectrum in a hollow cathode

The recording of the 0–0 band at 4240 Å ($^1\Pi$–$^1\Sigma$ transition) of the AlH molecule was made in a water-cooled hollow cathode of Schüler-Gollnow type (14). Our purpose was to investigate the suitability of the hollow cathode as a light source for direct registering, especially of band spectra and to get an idea of the sensitivity of the photomultiplier as compared with that of the photographic plate.

The use of the hollow cathode for exciting the band spectrum of AlH has been described by Nilsson (15). The carrier gas in the hollow cathode was helium, which was cleaned in a circulating system with a charcoal trap cooled by liquid air. All recording, both photo-electric and photographic was made with the same He-pressure (0.05 mm) and the same current (400 mA). No hydrogen was supplied from the outside to excite the AlH spectrum as there was enough enclosed in the aluminium of the cathode.

The constancy of the light-source was tested by fixing the cell on a hydride line and causing the recording drum to make a revolution (45^m). As is apparent from Fig. 5 a there are no disturbing short time fluctuations in the light source, which was driven on the 440-volt line with only a resistance as ballast. There is a continuous increase in intensity with a total of 4 % during the 45^m recording, which is probably explained by Fig. 5 b. In this record the liquid air trap was refilled immediately before starting the drum and then twice during the 45^m record. Such a refilling of the liquid air leads to a rapid decrease to a minimum followed by an increase, which after some time becomes linear. The continuous increase of intensity could probably have been totally avoided if a Dewar vessel of large diameter had been available at the time. With the one used there was a space of only a few mm between the trap and the vessel.

Fig. 6 shows the appearance of the AlH 0–0 band. The exposure, which has been photometrized in Fig. 6 c has been chosen so as to reflect the intensity course in the descending P-branch.

Fig. 7 and 8 show the final lines of the P-branch in photo-electric and photographic recording. The records have been made with different slit widths in order to show the gain in sensitivity with increasing slit widths in the photo-electric recording. The widths of the entrance and exit slits have been equal in all recordings. For very narrow slits a quadratic increase in sensitivity is to be expected with increased widths. As the slits are made wider the image of the entrance slit on the exit slit tends to be geometrical and the increase approaches linearity. For purposes of comparison corresponding slit widths were also used in the photographic exposures.

From the photo-electric recordings (Fig. 7) the gain in sensitivity with increasing slit widths is obvious. In drawing quantitative conclusions from the reproductions, those lines in the background which are caused by impurities in the carrier gas should be avoided. These lines may of course change considerably in intensity from time to time. The estimation of the sensitivity ratio in the different recordings should be made on lines which emanate from the cathode material. The increase in sensitivity is about 15 times when the slit is widened from 2/100 mm to 10/100 mm. In the recording with 10/100 mm there is a continuous background of about 1 mm.

The photographic exposures were made on Ilford Thin Film Half-Tone plates. As is to be expected there is no considerable increase in intensity with the slit width. Photograms of the exposures are reproduced in Fig. 8. As is apparent from the photogram in Fig. 9 even in a two hours exposure the background is almost entirely free from lines.

The sensitivity of the photo-electric recording (with RCA IP 21) in the range (4000–5000 Å) is generally spoken of as being of the same order as that of the photographic plate (Ilford Thin Film) with an exposure of some hours. This is true when the ideal slit widths are used. When the resolving power can be dispensed with, for instance, when searching for very weak lines in a pure spectrum, the sensitivity of the photoelectric recording may be raised considerably by using broader slits.

The direct recording method gives quickly very neat intensity diagrams. A disadvantage of the method is that it cannot be used for precission determinations of wavelengths and it has to be used chiefly as a valuable aid in addition to the photographic plate. As an excellent light source for direct recording, the authors recommend the hollow cathode because of its stability and its power to excite very pure and intense line and band spectra.

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